

The University of Chicago

I. "NORMAL" AND "ABNORMAL" ADDITION OF
HYDROGEN HALIDES

II. A CATALYTIC EFFECT OF METAL HALIDES
ON THE GRIGNARD REACTION

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1939

By

SARAH C. KLEIGER

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I. "NORMAL" AND "ABNORMAL" ADDITION
OF HYDROGEN HALIDES

Previous work from this laboratory has shown that in each case either of two possible products may be obtained by the addition of hydrogen bromide to propylene,¹ isobutene,² 1-butene,³ 1-pentene,⁴ allyl bromide,⁵ allyl chloride,⁶ 2-bromopropene,⁷ 2-chloropropene,⁸ vinyl chloride,⁹ vinyl bromide,¹⁰ and neopentylethylene.¹¹ The products formed when the reaction is carried out in the absence of oxygen and/or peroxides (in the presence or absence of an antioxidant) have been regarded as the "normal" addition products, while those formed in the presence of oxygen or peroxides have been designated the "abnormal" addition products. This paper discusses the difficulty of designating as "normal" or "abnormal" any given addition product of hydrogen bromide to trichloroethylene, 1-chloropropene, or 1-bromopropene, and proposes a solution of these and similar problems.

Trichloroethylene¹² does not react with hydrogen bromide

¹Kharasch, McNab, and Mayo, J. Am. Chem. Soc., 55, 2531 (1933); 56, 1425 (1934).

²Kharasch and Hinckley, ibid., 56, 1212 (1934).

³Kharasch and Hinckley, ibid., 56, 1423 (1934).

⁴Kharasch, Hinckley, and Gladstone, ibid., 56, 1642 (1934).

⁵Kharasch and Mayo, ibid., 55, 2468 (1933).

⁶Shane, "The Peroxide Effect upon the Addition of Hydrogen Bromide to Unsaturated Compounds (Unpublished Ph.D. dissertation, Dept. of Chemistry, University of Chicago, 1933).

⁷Kharasch, Engelmann, and Mayo, J. Org. Chem., 2, 288 (1937).

⁸Ibid.

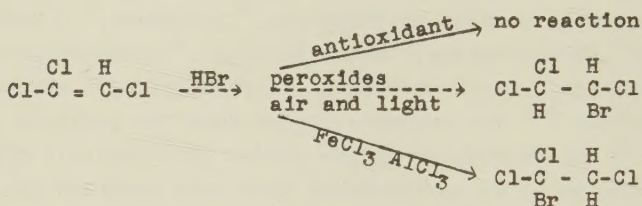
⁹Kharasch and Hannum, J. Am. Chem. Soc., 56, 712 (1934).

¹⁰Kharasch, McNab, and Mayo, ibid., 55, 2521 (1933).

¹¹Kharasch, Hannum, and Gladstone, ibid., 56, 244 (1934).

¹²Kharasch, Norton, and Mayo, J. Org. Chem., 3, 48 (1938).

in the presence of an antioxidant, even after several days at 100°. In the presence of anhydrous ferric or aluminum chloride, the unsymmetrical tetrahalide is formed readily, while in the presence of benzoyl peroxide, or of air and light, the symmetrical tetrahalide is obtained. The definition of the "normal" addition product may be open to some question in this instance because no uncatalyzed addition of hydrogen bromide in this substance has been observed.



Previous work on the addition of hydrogen bromide to the 1-halopropenes¹³ is summarized in Table 1. These results show

TABLE 1

THE ADDITION OF HYDROGEN BROMIDE TO THE 1-HALOPROPENES

Halogen Acid Added	Conditions	% 1,2-dihalide from 1-halopropene	
		Chloro	Bromo
HBr	Peroxides and/or air	100	100
HBr	Air absent, antioxidant present	40-80	90-100
HBr	Air absent, FeCl ₃ catalyst	0-10	67

that the 1,2-dihalides, exclusively, are formed in the presence of air or peroxides, that a smaller proportion of 1,2-dihalide is formed in the presence of an antioxidant, and still less in the presence of ferric chloride, a powerful catalyst for the "normal" addition reaction. The remainder of the addition product in each case is the isomeric 1,1-dihalide. The greater effectiveness of ferric chloride over the usual antioxidants in this case is of some importance, for in all previously-investigated cases they

¹³ Kharasch, Engelmann, and Mayo, op. cit.

could be used interchangeably (with respect to directive influence), except that the rate of reaction was greater with ferric chloride.

It was tentatively assumed, therefore, that products formed by the addition of hydrogen bromide to the 1-halopropenes in the presence of ferric chloride represent the "normal" addition products. This conclusion was further tested by experiments in which hydrogen chloride was added to the 1-halopropenes in the presence of anhydrous ferric chloride. Under such conditions both halogen acids added in the same manner.

The addition of hydrogen chloride is not complicated by an oxygen or peroxide effect^{14, 15, 16, 17} but it adds very slowly to many ethylene derivatives unless ferric chloride is used as a catalyst. (Aluminum chloride has the same effect as ferric chloride but often causes more tar formation.) In order that hydrogen chloride additions might be used as a standard for a "normal" addition, it therefore remained to be shown (1) that ferric chloride does not effect the direction of addition of either hydrogen chloride or hydrogen bromide, and (2) that the "normal" addition of hydrogen bromide corresponds to the addition of hydrogen chloride.

This work has now been completed and the author can state with certainty that ferric chloride affects only the rate, but not the course, of "normal" addition of hydrogen bromide and hydrogen chloride, both of which give corresponding products. It is her conclusion, therefore, that the addition of hydrogen chloride with or without ferric chloride, and the addition of hydrogen bromide with a ferric halide catalyst, are altogether equivalent to the "normal" uncatalyzed addition of hydrogen bromide. The author has been unable to find any exceptions to this principle in work done in this laboratory as well as work recorded in the literature.

¹⁴Kharasch and Mayo, unpublished work.

¹⁵Abraham and Smith, J. Chem. Soc., 1936, 1605.

¹⁶Rudovskii and Triefel, Org. Chem. Ind. (USSR), 2, 2035 (1936).

¹⁷Schöanberg, Ber., 70B, 2385 (1937).

Discussion of Results

It has already been mentioned that oxygen and peroxides have no observable effect on the direction of addition of hydrogen chloride to double bonds. The product formed in each case must therefore be the "normal" addition product. Table 2 shows that ferric chloride affects only the rate, and not the direction, of addition of hydrogen chloride to propene, isobutene, allyl chloride, 2-bromopropene, and 2-chloropropene. We conclude, therefore, that the "normal" addition products are obtained when hydrogen chloride is added to vinyl bromide, 1-chloropropene, 1-bromopropene, and trichloroethylene in the presence of ferric chloride. Furthermore, these data indicate that addition of hydrogen chloride to any ethylene derivative, with or without ferric chloride, gives only the "normal" addition product.

Table 2 also summarizes the results of the addition of hydrogen bromide to ten ethylene derivatives in the presence of ferric halides. In all cases, except those of 1-chloro- and 1-bromopropenes and of trichloroethylene, the addition products were identical with those obtained in the presence of antioxidants. Since, in all cases where comparisons are possible, these hydrogen bromide addition products also correspond to the hydrogen chloride addition products, they must necessarily be the "normal" addition products. Ferric salts must, therefore, catalyze the "normal" addition of hydrogen bromide as well as of hydrogen chloride.

Table 1 summarized previous work with the 1-halopropenes, which gave different proportions of addition products in the presence of antioxidants and ferric halides. Table 2 indicates that in the presence of ferric chloride, hydrogen bromide and hydrogen chloride add in the same manner to each halopropene. It is the author's belief, therefore, that in this instance, the addition products obtained in the presence of ferric chloride, rather than in the presence of antioxidants, represent the "normal" addition of halogen acids to these ethylene derivatives. In short, it now appears evident that in such addition reactions antioxidants and metallic halides are negative and positive catalysts respectively, and that their combined influence upon direction of addition is adequately explained by the facts that the former retard or suppress the "abnormal" addition reaction, whereas the latter accelerate the "normal" reaction. The previous conclusions of Kharasch,

TABLE 2

ADDITION OF HYDROGEN BROMIDE AND HYDROGEN CHLORIDE TO OLEFINS

Ref./Exp. No.	Olefine	Halogen Acid ^a	FeCl ₃ ^a	Reaction ^b Time Hrs.	Temp. °C	% Yield ^c Min. Max.	Product ^d
50	Propene	HBr 1.5	none	2	0	89	2-Bromopropene
49	Propene	HBr 1.2	.001	.25	-80	91	2-Bromopropene
5	Propene	HCl 1.5	none	144	0	48	2-Chloropropene
15	Propene	HCl 1.4	.001	48	-80	40	2-Chloropropene
46	Propene	HCl 1.5	.001	48	-80	60	2-Chloropropene
				24	0	97	
2	Isobutene ^e	HBr 1.5	not given			90	t.-Butyl bromide
51	Isobutene	HCl 1.0	.001	.08	-80	97	t.-Butyl chloride
52	Isobutene	HCl 1.5	none	6	-80	88	t.-Butyl chloride
5	Allyl bromide ^e	HBr 1.5	trace	18	room	29	94% 1,2-Dibromopropene ^f
5	Allyl bromide ^e	HBr 1.5	.007	17	room	100	1,2-Dibromopropene
5	Allyl bromide ^e	HBr 1.5	.007	16	room	100	1,2-Dibromopropene
31	Allyl bromide	HBr 1.5	.001	16	0	44	1,2-Dibromopropene ^g
41	Allyl bromide	HBr 1.5	.001	72	0	59	1,2-Dibromopropene ^g
28	Allyl bromide ^e	HBr 1.4	(FeBr ₃)	5	room	47	1,2-Dibromopropene ^g
5	Allyl bromide ^e	HCl 1.5	none	1426	room	≥0	1-Bromo, 2-chloropropene
12	Allyl chloride	HCl 1.5	none ^h	1488	room	≥0	1,2-Dichloropropene
17	Allyl chloride	HCl 2.5	none ^h	48	0	33	1,2-Dichloropropene
6	Allyl chloride	HCl 1.5	.001	432	room	79	1,2-Dichloropropene
				72	0	83	
11	Allyl chloride	HCl 1.4	.001	144	room	85	1,2-Dichloropropene
				168	room		

TABLE 2 - Continued

Ref./Exp. No.	Olefine	Halogen Acid ^a	FeCl ₃ ^a	Reaction ^b		% Yield ^c		Product ^d
				Time Hrs.	Temp. °C	Min.	Max.	
30	2-Bromopropene	HBr 1.5	.001	48	room	94	94	2,2-Dibromopropene
40	2-Bromopropene	HBr 1.6	.001 (FeBr ₃)	22	0	94	98	2,2-Dibromopropene
8	2-Bromopropene	HCl 1.6	none	1826	room	63	70	2-Bromo,2-chloropropene
39	2-Bromopropene	HCl 1.5	none	2640	room	68	75	2-Bromo,2-chloropropene
25	2-Bromopropene	HCl 1.5	.001	72	0	65	74	2-Bromo,2-chloropropene
26	2-Chloropropene	HCl 1.5	.001	48 120	0 room	77	94	2,2-Dichloropropene
10	Vinyl bromide ^e	HBr 1.6	.019	24	room	88	>101	1,1-Dibromoethane
54	Vinyl bromide	HCl 1.5	none	1296	room		c.601	
53	Vinyl bromide	HCl 1.5	.001	1	room			
29	Vinyl chloride	HBr 1.4	.001	24	0	77	93	1-Chloro, 1-bromoethane
45	Vinyl chloride	HBr 1.4	.001	48 24	room 0	86	95	1-Chloro, 1-bromoethane
3	Vinyl chloride	HCl 1.5	none	504	room	>10		1,1-Dichloroethane
1	Vinyl chloride	HCl 1.3	.001	48 148	0 room	57	62	1,1-Dichloroethane
13	Vinyl chloride	HCl 1.4	.001	120	room	59	77	1,1-Dichloroethane
18	Vinyl chloride	HCl 1.4	.001	72	room	71	84	1,1-Dichloroethane
19	Vinyl chloride	HCl 1.5	.001	72	room	71	82	1,1-Dichloroethane
12	Trichloroethylene ^e	HBr 1.5	.005	24	room	73		1,1,2-Trichloro, 1-bromoethane
12	Trichloroethylene	HBr 1.1	.004	24	room	81		1,1,2-Trichloro, 1-bromoethane
12	Trichloroethylene	HCl 1.6	.003	144	room	42		1,1,1,2-Tetrachloroethane

TABLE 2 - Continued

Ref./Exp. No.	Olefine	Halogen Acid ^a	FeCl ₃ ^a	Reaction ^b Time Hrs.	Temp. °C	% Yield ^c Min. Max.	Product ^d
37	1-Bromopropene ^e	HBr 1.8	.003	1.4	0	96	59% 1,2-Dibromopropene
7	1-Bromopropene ^e	HBr 1.6	.006	2	0	90	67% 1,2-Dibromopropene
7	1-Bromopropene ^e	HBr 1.6	.01	.75 ^j	0	91	67% 1,2-Dibromopropene
7	1-Bromopropene ^e	HCl 1.6	.16	15	0	61	65% 1-Bromo, 2-chloropropene
7	1-Bromopropene ^e	HCl 1.5	.003	24	0	75	64% 1-Bromo, 2-chloropropene
7	1-Chloropropene ^e	HBr 1.6	.006	2	room	15	1-Chloro, 1-bromopropene
7	1-Chloropropene ^e	HBr 1.6	.003	3	room	83	1-Chloro, 1-bromopropene
7	1-Chloropropene ^e	HBr 1.6	.018	13	room	91	1-Chloro, 1-bromopropene
22	1-Chloropropene ^e	HCl 1.5	.001	72	room	55	1,1-Dichloropropene
7	1-Chloropropene ^e	HCl 2.0	.04	48	room	90	1,1-Dichloropropene

^aExpressed in moles per mole of olefine. In all cases 0.1 moles of ethylene derivative was used.

^bAll reactions were performed in the dark.

^cThe "minimum" yield is calculated from the weight of pure dihalide isolated after the final distillation. Low yields are often due to losses from incomplete condensation in vacuum distillation. "Maximum yields" are calculated on the basis of the crude reaction product after removal of solvent, catalyst, hydrogen halide and unreacted olefine.

^dThese products are the normal addition products. In those cases where percentages are given, the remainder was the other possible addition product.

^eIndicates experiments using the vacuum technique of Kharasch and Mayo. Pressures of 10⁻³ - 10⁻⁴ were used.

^fPercentage of 1,2-dihalide was recalculated using the corrected index of refraction: 1.5200. Large amounts of tar formed during the reaction account for the low yields.

^gOne and one-half moles of nitromethane were used as solvent in this experiment. It is of interest to note that addition is accelerated by the presence of a solvent of high dielectric constant. ^hAll attempts to add hydrogen chloride to vinyl bromide yielded products having no sharp boiling point, indicating that halogen exchange had taken place.

^jComplete in five minutes.

Engelmann, and Mayo¹⁸ are thus confirmed and extended. Similar reasoning leads to the conclusion that the unsymmetrical halide obtained from trichloroethylene in the presence of ferric halides must be the "normal" addition product, although no uncatalyzed addition has yet been observed.

Experimental

All experiments except numbers 35, 37, and 47 were performed in the presence of air. The anhydrous ferric chloride was weighed in the bomb tube, the olefine added, and the halogen acid was passed in at -80° until a sufficient quantity had been absorbed. The bomb was then sealed off and allowed to stand in the dark until the reaction was complete. The bombs were shaken at intervals to insure contact of their contents with the ferric chloride.

When the reaction was complete, the bomb was cooled to -80° and opened. The excess hydrogen halide was allowed to escape, and the reaction products were distilled from the catalyst and tar at 15-25 mm., the distillate being collected at -80° . The halides were then dried over anhydrous potassium carbonate and fractionally distilled through an efficient column. The composition of the addition products was determined by their boiling points and refractive indices, most of which had been recorded previously in papers from this laboratory.

Experiments number 35, 37, and 47 were carried out according to the vacuum technique of Kharasch and Mayo.¹⁹

Summary

1. The addition of hydrogen bromide and hydrogen chloride to several ethylene derivatives has been studied in the presence and absence of ferric chloride as catalyst.

2. The direction of addition of hydrogen chloride is the same as that of the "normal" addition of hydrogen bromide.

¹⁸Op. cit.

¹⁹Op. cit.

II. A CATALYTIC EFFECT OF METAL HALIDES

ON THE GRIGNARD REACTION

The reaction of Grignard reagents with aldehydes and ketones has long been of interest because of the "abnormal" reducing action of certain organomagnesium compounds upon the latter substances, the products being the primary and secondary alcohols respectively.¹ Moreover, studies^{2, 3, 4, 5} of the effect of Grignard reagents on benzophenone have shown that up to 10 per cent of benzopinacol may be found in the reduction products. This unusual result has been explained by the presence of metallic magnesium in the reaction mixture during the addition of the ketone, producing conditions similar to those for the preparation of pinacols from a ketone and the system Mg-MgI₂. Careful exclusion of the metal through the use of clear, filtered Grignard solutions verified this interpretation. Under such conditions no benzopinacol was found in spite of careful search for this compound.^{6, 7, 8}

Both Bachmann⁹ and Gilman and Fothergill¹⁰ have shown that

¹Kharasch and Weinhouse, J. Org. Chem., 1, 209 (1936). This paper summarizes and interprets the reducing action of Grignard reagents on ketones. For a more complete literature review see the Ph.D. dissertation of S. Weinhouse, "The Reducing Action of Grignard Reagents," Dept. of Chemistry, University of Chicago, 1936.

²Schmidlin, Ber., 39, 4198 (1906).

³Lagrange, Ann. de Chim., (10) 8, 363 (1927); J. Gen. Chem., (USSR) 6, 1766 (1936); Chem. Abstr., 31, 4308 (1937).

⁴Arbuzov and Arbuzova, J. Gen. Chem., (USSR) 2, 388 (1932); Chem. Abst., 27, 974 (1933).

⁵Davies, Nixon and Jones, J. Chem. Soc., 1930, 1916.

⁶Blicke and Powers, J. Am. Chem. Soc., 51, 3378 (1929).

⁷Noller, Grebe and Knox, J. Am. Chem. Soc., 54, 4690 (1932).

⁸Kharasch and Weinhouse, op. cit.

⁹Bachmann, J. Am. Chem. Soc., 53, 2758 (1931).

¹⁰Gilman and Fothergill, J. Am. Chem. Soc., 51, 3149 (1929).

excellent yields of benzopinacol may be obtained by the treatment of ketones with filtered solutions of triphenylmethylmagnesium bromide. The deep color of the solution and the isolation of triphenylmethyl peroxide indicate the presence of free radicals in such solutions.

The present investigation was undertaken to determine the effect of metals other than magnesium on the course of reaction between aliphatic Grignard reagents and benzophenone. Before attempting to study the effect of metals or their halides on any Grignard reaction, it is necessary to know what impurities are to be found in the magnesium used for the preparation of the reagent. The author therefore submitted to Dr. W. C. Pierce and Mr. W. W. Marshall of this laboratory three samples of magnesium for spectrographic analysis. The first sample was ordinary magnesium turnings obtained from Mallinckrodt and taken to be representative of the metal available in this country. The second was magnesium prepared for Grignard reactions by Kahlbaum. This we believed would be typical of the metal used abroad. The third sample was sublimed magnesium obtained through the courtesy of the Dow Chemical Company.¹¹ The report of the analysts is as follows:

Arc spectra for the three samples of magnesium submitted are shown in the inclosed plate (see Figure 1). Two spectra were photographed for each sample in the wave length region 2500-3450Å.

The following impurities were found. The concentrations given are only approximations, based on the appearance of the lines.

Sample	% Mn	% Cu	% Sn	% Fe	% Ag	% Pb
Mallinckrodt	0.05-0.1	0.01	0.01	0.01		
Kahlbaum	0.1	0.01	0.01	0.001	0.001	
Dow						0.01

A colorimetric analysis of the Kahlbaum magnesium gave 0.057% manganese.

It is readily apparent from a study of this report that in any experiment where the effect of one metal halide upon a Grignard reaction is to be studied, the reagent must be prepared from the sublimed magnesium.

Filtered solutions of the organo-magnesium halide were pre-

¹¹The author wishes to express her appreciation to the Dow Chemical Co. for the gift of a kilogram of sublimed magnesium, and to Dr. Pierce and Mr. Marshall for their analysis of these samples.

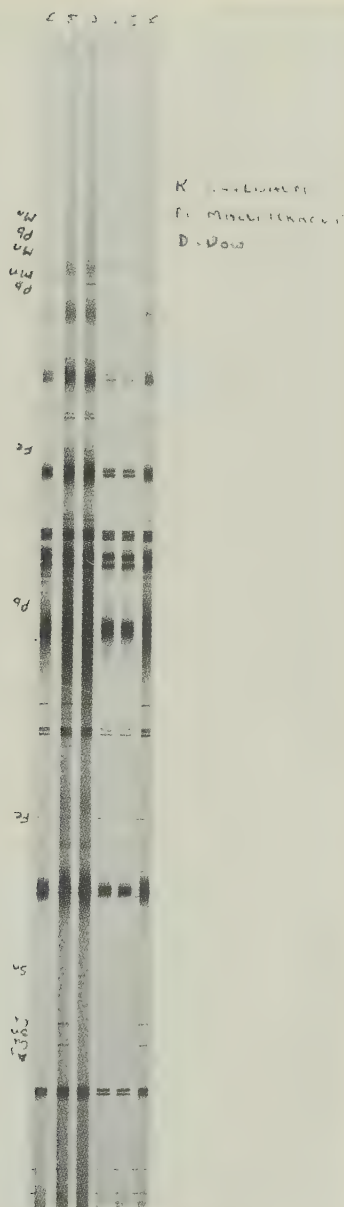


FIG. 1.--SPECTROGRAPHIC ANALYSIS OF MAGNESIUM

pared from sublimed magnesium. To portions of these reagents weighed amounts of anhydrous cuprous chloride, chromic chloride or manganous chloride were added and the results compared with experiments in which no heavy metal salt was added. The above mentioned metal halides were chosen because the first two are known to catalyze specific reactions of Grignard reagents^{12, 13} and the last because manganese is the impurity found in largest amounts in ordinary magnesium turnings.

When a filtered solution of isobutylmagnesium bromide is treated with benzophenone in benzene, a dense precipitate of the magnesium bromide salt of benzhydrol, equivalent to a 91 per cent yield, is obtained. When 0.1-1.0 mole per cent of anhydrous cuprous chloride is added to the filtered Grignard reagent, a vigorous reaction occurs and a precipitate of finely divided metallic copper is obtained. If to this resultant mixture the ketone is added, the course of reaction is identical with that observed with the original clear Grignard reagent. Upon addition of the benzene solution of benzophenone the benzhydrol salts precipitates, the supernatant liquid clears, and on analysis the yield of benzhydrol is found to be the same as when the clear Grignard reagent is used. These facts indicate that the presence of finely divided copper has no apparent catalytic effect in this reaction (see Table 1).

However, if the same amounts of manganous chloride are added in place of the copper halide, an entirely new phenomenon is

¹²Linn and Noller, *J. Am. Chem. Soc.*, **58**, 816 (1936). These authors show that small amounts of cuprous chloride catalyze the disproportionation reaction between ethylmagnesium bromide and ethyl bromide. They further prove that it is not the salt itself, but rather the highly reactive copper, formed by the interaction of cuprous chloride and the Grignard reagent, which is the actual catalyst for the reaction. The addition of copper, freshly prepared by the reduction of copper oxide with hydrogen is just as effective in initiating the formation of ethylene and ethane.

¹³Job and Cassal, *Bull. soc. Chim.* (4), **41**, 814 (1927). These workers report that carbon monoxide reacts with phenylmagnesium bromide only in the presence of small amounts of chromic chloride. With carefully purified materials, carbon monoxide is absorbed by the Grignard in the presence of chromic chloride in the range between -15° and the boiling point of ether. Below -15° no absorption takes place, and it is significant that at this temperature an exothermic reaction between the Grignard reagent and the heavy metal halide takes place.

observed. After the isobutylmagnesium bromide and the heavy metal salt have reacted, the mixture is black due to suspended manganese.¹⁴ The addition of a few drops of ketone solution turns the reaction mixture a deep cherry red, characteristic of magnesium ketyls. The color persists throughout the addition of the benzophenone and on hydrolysis benzopinacol is isolated. The same color is observed during the preparation of pinacols by the reduction of ketones with Mg-MgI_2 , and here too is attributed to the presence of the ketyl radical.

TABLE 1

THE EFFECT OF CUPROUS CHLORIDE ON THE ADDITION OF
BENZOPHENONE TO ISOBUTYLMAGNESIUM BROMIDE

Mole % CuCl	% Benzhydrol
0.0	91.8*
0.1	91.6*
0.25	91.2*
0.5	91.3*
0.75	90.5*
1.0	90.1*

*Indicates that the value is the average of two or more experiments, which did not vary by more than 2 per cent.

The amount of pinacol was found to vary directly with the proportion of manganous chloride added. When only 0.1 mole per cent of salt is introduced into the reaction, the yield of pinacol is low (32%) and large amounts of benzhydrol are isolated. Increasing the amount of manganous chloride to one mole per cent results in almost complete suppression of benzhydrol and increase in the yield of benzopinacol to 89 per cent (see Table 2, Figure 2).

Substituting isobutyl chloride for the bromide has no effect on the yield obtained in the control reaction, but lowers the amount of pinacol formed in the presence of one mole per cent of manganous chloride to 51 per cent. This may be partially explained by the slower rate of reaction between the metal halide and the Grignard reagent. Isoamylmagnesium chloride gives under the same conditions 34 per cent addition product and 50 per cent reduction of which 12.5 per cent is benzopinacol.

¹⁴Hoffman, Ber. 56, 1124 (1928).

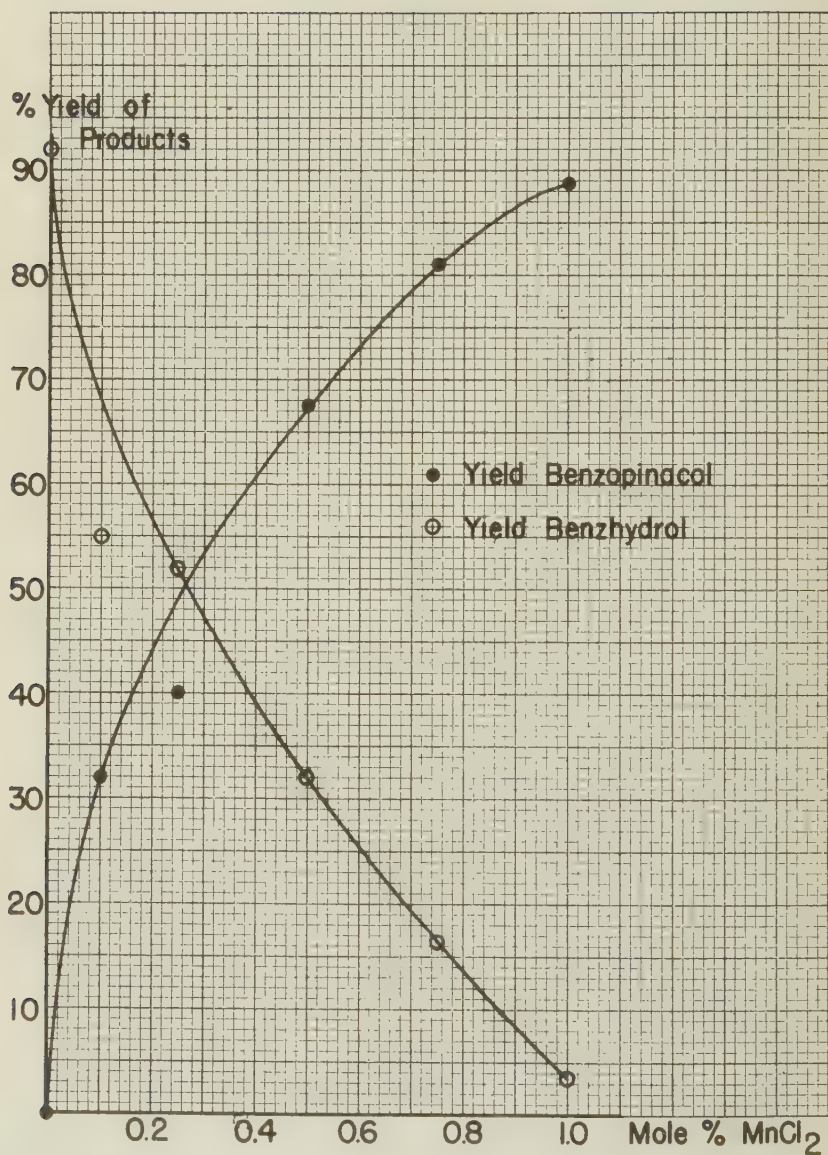


Fig.2-- Effect of MnCl_2 on Ratio of Products

TABLE 2

THE EFFECT OF MANGANOUS CHLORIDE ON THE ADDITION OF
BENZOPHENONE TO ISOBUTYLMAGNESIUM BROMIDE

Mole % MnCl_2	% Benzhydrol	% Benzopinacol	Total %
0.0	91.8	0.0	91.8*
0.1	55.0	32.0	87.0
0.25	51.9	39.8	91.7
0.5	31.5	67.1	98.6*
0.75	16.5	80.7	97.2*
1.0	3.2	88.2	91.4*
2.0	2.2	92.0	94.2

*Indicates that the values given in these experiments are the average of two or more experiments, which did not vary by more than 3 per cent.

The effect of chromic chloride is intermediate between that of cuprous chloride and manganous chloride. Though benzopinacol is formed (see Table 3, Figure 3), the amount is much lower than is obtained with corresponding amounts of manganous chloride, and even with two mole per cent of chromic chloride appreciable amounts of benzhydrol are obtained.

TABLE 3

THE EFFECT OF CHROMIC CHLORIDE ON THE ADDITION OF
BENZOPHENONE TO ISOBUTYLMAGNESIUM BROMIDE

Mole % CrCl_3	% Benzhydrol	% Benzopinacol	Total %
0.0	91.8	0.0	91.8*
0.1	82.4	3.5	85.9*
0.25	75.2	10.4	85.6
0.5	66.5	21.6	88.2*
0.75	52.0	32.0	84.0*
1.0	16.0	46.6	62.6*
2.0	11.2	61.3	72.5

*Indicates that the value given in these experiments are the average of two or more experiments, which did not vary by more than 3 per cent.

One experiment in which ferric chloride was tried as catalyst for the reaction of benzophenone and isobutylmagnesium bro-

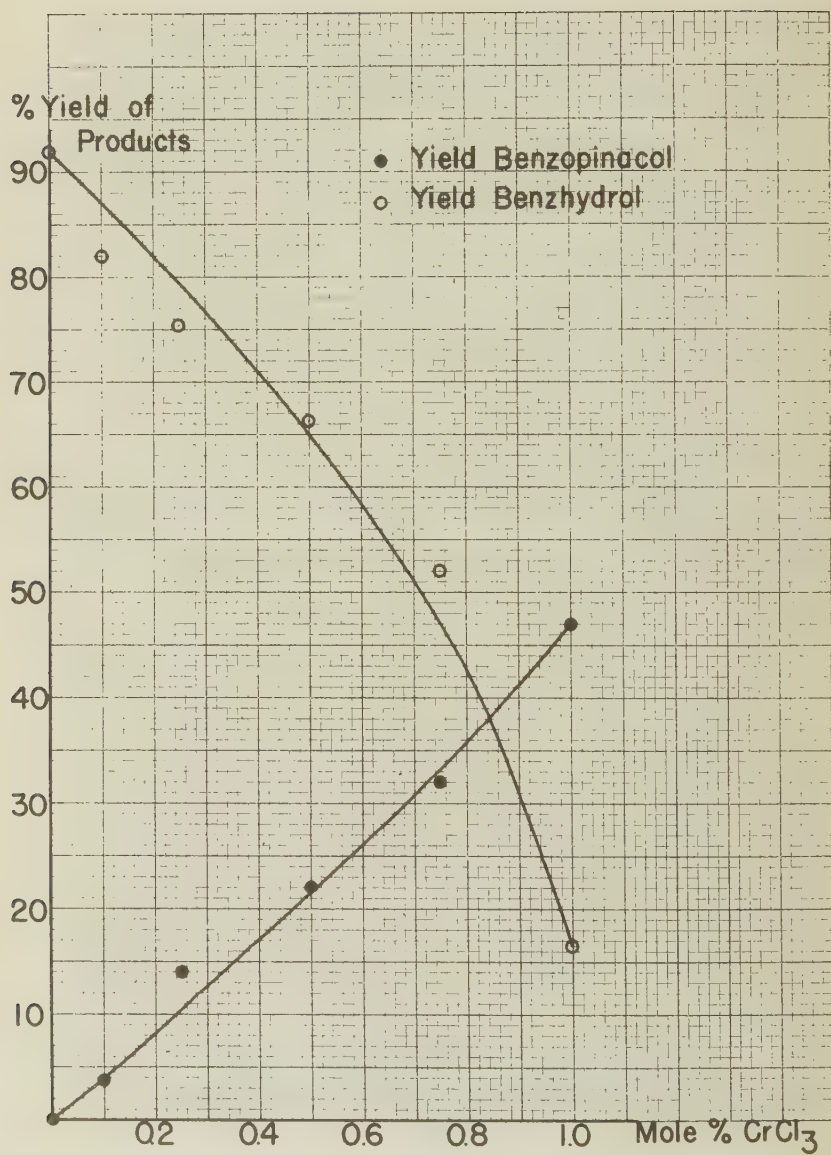


Fig.3-- Effect of CrCl_3 on Ratio of Products

mide was performed. Using two mole per cent of the salt, a 71 per cent yield of benzopinacol was obtained, indicating that iron is comparable to chromium in its catalytic effect. An attempt to prepare pinacol itself by the action of isobutylmagnesium bromide and one mole per cent of manganous chloride on acetone was unsuccessful; only the addition product was isolated.

The amount of metal halides (manganous chloride, cuprous chloride, chromic chloride, ferric chloride) initially used in the experiments was 0.1 mole per cent. This was raised to 0.25 mole per cent and the quantity thereafter increased by 0.25 mole per cent in subsequent series of experiments until one mole per cent was reached. One set of experiments with two mole per cent was then performed. At this level the maximum catalytic effect had already been reached with manganese, as shown by the fact that twice as much of the catalyst did not perceptibly affect the end products. In the case of chromic chloride, on the other hand, increasing quantities of catalyst were still capable of changing the course of reaction, even at the two mole per cent stage. The effect of larger amount was never investigated because of the excessive destruction of the Grignard reagent by the catalyst with consequent lowering of the overall yield.

The data presented suggest that the reduction of benzophenone by a Grignard reagent may proceed in either one of two ways. The reaction may involve the transfer of an electron pair, leading to the formation of benzhydrol; or it may depend upon the exchange of a single electron, which leads to the production of benzopinacol. The last reaction is, no doubt, a chain reaction since such small amounts of metal halide are necessary to produce large yields of benzopinacol.

The formation of pinacols by this new technique seems to be limited in scope. Since acetone could not be reduced to pinacol, it appears that only those ketones which are usually reduced by Grignard reagent may be used.

Experimental

The organic compounds used were obtained from the Eastman Kodak Company and were distilled or crystallized before use. The cuprous chloride was freshly made; the anhydrous manganous chloride was prepared from the hydrated form by heating in an oven

for eight hours at 120° ; the chromic chloride and ferric chloride were the usual anhydrous reagent. Only sublimed magnesium was used in the preparation of the Grignard reagent.

Preparation of the Grignard reagent.--The Grignard reagent was prepared in a three-necked flask equipped with mercury-sealed stirrer, reflux condenser and dropping funnel, the latter two fitted with calcium chloride tubes to exclude moisture from the reaction. A narrow tube filled with glass wool and ending in a stopcock was attached to the side of the flask.

A 10 per cent excess of sublimed magnesium was placed in the flask and approximately one-third (0.8 mole) of the anhydrous ether to be used was added. The alkyl halide (0.4 mole) was dissolved in the remainder of the ether (1.6 mole). After running in a few drops of the halide solution, the reaction mixture was warmed with a micro burner until reaction started. The remainder of the halide solution was then added at such a rate as to keep the ether refluxing gently. After addition of the halide was complete, the reaction mixture was refluxed for an additional half hour with continuous stirring and allowed to cool.

The Grignard reagent was then filtered through the glass wool plug into a graduated dropping funnel and a two milliliter aliquot removed for titration. The remaining Grignard reagent was divided into three equal parts and transferred to three-necked flasks, each fitted with a reflux condenser, mercury-sealed stirrer, dropping funnel and calcium chloride tubes.

To two of the three portions of the solution weighed quantities of anhydrous metal halide were added; the third lot was used as a control. Upon addition of the heavy metal salt, a vigorous exothermic reaction occurred and the solution turned black. Where isobutyl chloride or isoamyl chloride were used the reaction was not so rapid, and it was necessary to warm the mixture slightly to insure complete interaction between the metal halide and the Grignard reagent.

Addition of benzophenone.--The calculated amount of ketone in six times its weight of benzene was added dropwise to each portion of the Grignard reagent over a period of one and one-half hours while the reaction mixture was kept cold in a bath of ice and water. After all the ketone had been added, the temperature was allowed to rise to that of the room and stirring continued for an additional hour.

Isolation of product.--The precipitate of the magnesium salt of benzhydrol was collected on a filter from the ether-benzene mixture, washed with benzene, dried, weighed and then hydrolyzed with 10 per cent sulfuric acid. The benzhydrol was crystallized from dilute alcohol and was found to melt at 65-67°.

The ether-benzene filtrate was treated at 0° with ice-cold 10 per cent sulfuric acid and dried over anhydrous potassium carbonate. The solvent was then removed on a steam bath. Only a small amount of oil was obtained at this point from those experiments in which either no metal halide or cuprous chloride had been used. When, however, manganous chloride or chromic chloride was the added catalyst, a residue of benzopinacol remained. After crystallization from alcohol the product melted at 176-178° with decomposition.

Summary

1. The effect of some heavy metal halides on the reaction of Grignard reagents with benzophenone has been studied.

2. It has been shown that cuprous chloride has no catalytic effect; manganous chloride is a potent catalyst for the formation of benzopinacol; and chromic chloride and ferric chloride are intermediate in their catalytic power.

3. The reaction apparently is not general, but can only be applied to those ketones which are reduceable by Grignard reagents.

